On the Refractive Indices of Mercury and Thallium Vapours.

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1. *Introduction.*

Although numerous accurate and extended determinations have been made of the refractive indices of gases which exist as such at ordinary temperatures, few have been made with the vapours of elements or compounds which, at room temperatures, are solids and possess a low equilibrium vapour pressure in that state.

Notable among the latter are the determinations made by Prof. R. W. Wood* with sodium vapour and those made by Messrs. C. Cuthbertson and E. Parr Metcalfe† with the vapours of sulphur, phosphorus, mercury, zinc, cadmium, selenium, and tellurium. In the work of both of these investigations an interference method was adopted. In Wood's a Michelson interferometer was used and in Cuthbertson and Metcalfe's one of the Jamin type. For the investigation of Cuthbertson and Metcalfe the glass interferometer tubes ordinarily used with Jamin interferometers were wholly unsuitable. These, as is well known, are provided with plane parallel plate glass ends ground in and luted with shellac or a wax having similar properties, and when heated to 300° C. or higher, the shellac chars and the tubes frequently crack, soften, or become distorted. For these reasons Cuthbertson and Metcalfe had recourse to interferometer tubes made of fused silica which were made, with great skill, by Messrs. Heraeus, of Hanau. The ends of the tubes through which the interfering rays passed were plates of quartz ground optically flat, fused into the tubes and again polished. In their manufacture such tubes are, however, difficult to make. Failures are frequent and consequently the tubes are expensive. On this account investigators have been deterred hitherto from studying the refractivities of the vapours of metals and other substances, having moderately high melting points and vapourising temperatures.

A short time ago the writer found that hollow prisms of any angle with optically flat faces, and interferometer tubes with plane parallel end-plates, could be made with ease and at a low cost out of clear fused quartz. These were tried out with mercury vapour and results obtained which showed a good agreement with the values recorded by Cuthbertson and Metcalfe for this metal.

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* Prof. R. W. Wood, 'Phil. Mag.,' September, 1904.

† Messrs. C. Cuthbertson and E. Parr Metcalfe, 'Phil. Trans.,' A, vol. 207, p. 135 (1908).

As no determinations appeared to have been made with thallium vapour, and as it gave promise of interesting results, an attempt was made to measure the refractive indices of this element for a number of wave-lengths. No practical difficulties were experienced in working with this metal, and, from the success which accompanied the attempt, it would appear that, with the use of the fused quartz apparatus referred to above, the refractive indices of metals having a moderately high melting point can be determined with as much ease as those of an ordinary gas.

2. *Fused Silica Prisms and Interferometer Tubes.*

The method followed in making up hollow silica prisms and interferometer tubes was based on the work of Messrs. R. G. Parker and A. J. Dalladay,* who found that optical parts of silica when placed in contact would fuse together if heated to a temperature somewhat below 1200° C.—the point of devitrification. In applying this principle, however, it was found that unless special precautions were taken it was extremely difficult to attach plane parallel end-plates to interferometer tubes or face plates to prisms, with an oxy-gas or oxy-hydrogen blowpipe, without distorting the plates and without coating the surfaces exposed to the flame with a thin layer of devitrified silica. These difficulties were, however, readily overcome by adopting a procedure first used by Messrs. Gibson and Argo.† Figs. 1 and 2 will serve to illustrate the method adopted.

A tube AB, fig. 1, of clear fused silica from 1·0 to 1·5 cm. in diameter was first of all selected, care being taken to have the bore as uniform as possible.

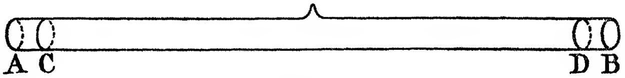

Fig. 1.

Two discs, C and D, were then cut from a plate of clear fused quartz which had been worked optically flat and these were carefully ground to a diameter the same as that of the bore of the interferometer tube. The discs were then inserted in the tubes, as shown in the diagram, at from two to three centimetres from the ends of the tube, and were held at right angles to the axes of the tube by means of two projection lamp carbons with plane ends. The finely pointed flame of an oxy-hydrogen blowpipe was then directed in the plane of the disc against the outside of the tube, until the wall of the latter slightly softened. By means of the pointed end of an ordinary file the softened tube wall was then gently pressed against the edge of the disc, when adhesion was readily obtained. To obtain adhesion all round the disc it was only necessary to heat the tube point by point all round its circumference. After this was done, it was generally advisable to rotate the tube slowly for a short time with the line of union just within the pointed end of the flame. By following this method, by which the flame did not come in contact with the discs, it was found that interferometer tubes could be readily, easily and cheaply made, with end plates beautifully clear and without any trace of distortion, except close to the edges.

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* Parker and Dalladay, 'Chem. News,' December 29, 1916, p. 310.

† Gibson and Argo, 'Jl. Am. Chem. Soc.,' vol. 40, No. 9, p. 1327, September, 1918.

Fig. 2 will indicate the procedure adopted in making up the hollow prisms. In this case the discs were ground in the shape of ellipses, the dimensions of the latter being determined by the refracting angles selected for the prism and the diameter of the tube used. The procedure followed in effecting union between the edges of the discs and the wall of the tube was precisely the same as that followed in making up the interferometer tubes. After the prism was made, the projecting portions of the main tube were cut off so as not to interfere with the rays entering or leaving the prism.

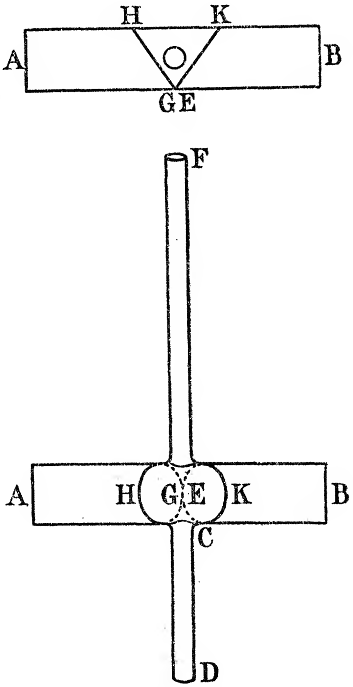

FIG. 2.

3. *Interferometric Determinations.—Theory.*

The theory for the determination of the refractive indices of a vapour by means of the Jamin interferometer is well known, and may be summarised as follows :—

Let ρ_1 be the density of the saturated vapour at temperature t_1,
ρ_2 ” ” ” ” t_2,
ρ_0 be a selected standard density of the vapour.

Let μ_1, μ_2, μ_0 respectively be the refractive indices of the vapour corresponding to the densities ρ_1, ρ_2, ρ_0 for a selected wave-length.

Let λ_0 be the wave-length of the selected light *in vacuo*, and λ_1, λ_2 the wave-lengths of the same radiation in the vapour at the densities ρ_1 and ρ_2.

Let L be the length of the interferometer tube and x be the number of interference bands which pass a fiducial mark during the evaporation or condensation.

Then $$L = n_1\lambda_1 = n_2\lambda_2 \quad \text{where} \quad n_1 - n_2 = x,$$

$$\lambda_1 = \frac{\lambda_0}{\mu_1}, \qquad \lambda_2 = \frac{\lambda_0}{\mu_2},$$

$$\therefore \quad L = \frac{n_1\lambda_0}{\mu_1} = \frac{n_2\lambda_0}{\mu_2} = \frac{n_1 - n_2}{\mu_1 - \mu_2}\lambda_0,$$

$$\therefore \quad \mu_1 - \mu_2 = \frac{x\lambda_0}{L}.$$

But $$\frac{\mu_1 - 1}{\rho_1} = \frac{\mu_2 - 1}{\rho_2} = \frac{\mu_0 - 1}{\rho_0} = \frac{\mu_1 - \mu_2}{\rho_1 - \rho_2},$$

$$\therefore \quad \mu_0 - 1 = \frac{x}{\rho_1 - \rho_2} \frac{\lambda_0\rho_0}{L},$$

from which it follows that $x/\rho_1 - \rho_2$ should be constant, for any two selected densities of the vapour.

4. *Interferometer Experiments with Mercury Vapour.*

In these experiments the interferometer tubes, one of which contained a quantity of mercury, were enclosed in an electric furnace made of nichrome wire wound on a cylinder of sheet rolled asbestos. This furnace was placed between the mirror plates of the interferometer, and the tubes in it were adjusted in position so that the fringe system was clearly visible. The furnace was gradually heated, and the temperatures were ascertained by means of a carefully calibrated glass thermometer. The temperature was controlled by a rheostat in the heating circuit, and no difficulty was experienced in maintaining the tubes at any desired temperature.

Table I.

Temperature.	Density of saturated Hg vapour.
° C.	grm./c.c.
100	0·0000021
110	0·0000040
260	0·0005830
270	0·0006528
280	0·0008645
300	0·0013466
305	0·0013882
310	0·0016447
320	0·0019879

The densities of the saturated mercury vapour for different temperatures were determined by interpolation from values recorded by F. B. Jewett,* and are given in Table I.

The standard density selected was that of mercury vapour reduced to 0° C. and 76 cm. pressure, on the assumption that it obeyed the ordinary gas laws.

i.e.,
$$\rho_0 = \frac{\text{density of hydrogen at N.T.P.} \times \text{At. wt. of mercury}}{\text{molecular wt. of hydrogen}}$$
$$= \frac{0{\cdot}0000899 \times 200{\cdot}6}{2{\cdot}002}$$
$$= 0{\cdot}009001 \text{ grm./c.c.}$$

This, of course, is based on the assumption that mercury vapour is a monatomic gas. The lengths of the interferometer tubes were 26·0 cm., and were taken to be constant over the range of temperatures covered, since for a change of 300° C. the increase in length was not more than 1 part in 6000.

The results obtained with wave-length λ = 6230 Å.U., which are typical of those obtained with other wave-lengths, are given in Table II.

Table II.

Wave-length λ = 6230 A.U.

Initial temperature.	Final temperature.	$\rho_1-\rho_2$.	x.	$k = \dfrac{x}{\rho_1-\rho_2}$.	Mean value.
° C.	° C.				
110	322·5	0·002080	8·5	4090	
110	320·0	0·001984	8·0	4030	
110	322·0	0·002060	8·4	4080	Mean k = 4078.
110	322·0	0·002060	8·2	4000	
110	324·0	0·002139	9·0	4210	
110	322·5	0·002080	8·4	4040	μ_0-1 = 0·000882.
110	322·5	0·002080	8·5	4090	
110	322·0	0·002060	8·4	4080	
110	322·0	0·002060	8·4	4080	

The refractive indices obtained with the four wave-lengths, λ = 4860 Å.U., λ = 5132 Å.U., λ = 6110 Å.U., and λ = 6230 Å.U., are given in the fourth column of Table III.

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* F. B. Jewett, 'Phil. Mag.,' November, 1902, p. 546.

Table III.—Refractivity of Metallic Vapours.

Mercury of normal pressure and temperature.					
Jamin interferometer by Cuthbertson and Metcalfe.		Jamin interferometer by author.		Quartz prism by author.	
Wave-length λ Å.U.	Refractive index, μ_0.	Wave-length λ Å.U.	Refractive index, μ_0.	Wave-length λ Å.U.	Refractive index, μ_0.
5183	1·000943	4860	1·000949	4358·56 Hg	1·000942
5460·97 Hg	1·000941	5132	1·000943	5460·97 Hg	1·000902
5893 Na	1·000933	6110	1·000924	5780 Hg	1·000891
6563·04 Hα	1·000899	6230	1·000882	6234·31 Hg	1·000860

Thallium at temperature of 540° C. (German silver and copper thermo-couple).	
Quartz prism by author.	
Wave-length λ A.U.	Index of refraction μ.
4358·56 Hg	1·000229
4861·49 Hβ	1·000110
5460·97 Hg	1·000293
5769·45 Hg	1·000222
5790·49 Hg	1·000144
5893 Na	1·000165
6234·31 Hg	1·000309
6563·04 Hα	1·000142

The results of Cuthbertson and Metcalfe, reduced to the same standard density, are given in the second column of the same table, and it will be seen the two sets of values present a fair agreement.

5. *Prism Experiments with Mercury Vapour.*

In carrying out this set of experiments with mercury vapour, one of a number of prisms which had been made up was selected at random. Its refracting angle, which was large, was 93·5°. A quantity of mercury was put into the prism sufficient to fill the lower tube and part of the prism itself. The prism was then exhausted and hermetically sealed. It was then enclosed in an electric furnace of nichrome wire, temperatures being measured in this case with a thermo-couple of copper and German silver, which was carefully calibrated. The readings were taken with a milli-voltmeter. The prism and furnace were mounted on a table of a finely constructed refractometer, with which readings could be taken to 1 second of arc.

As the deviations obtained were small, the ordinary formula for minimum deviation was modified as follows :—

$$\mu = \frac{\sin \mathrm{A}+\mathrm{D}/2}{\sin \mathrm{A}/2} = \frac{\sin \mathrm{A}/2 \cos \mathrm{D}/2+\cos \mathrm{A}/2 \sin \mathrm{D}/2}{\sin \mathrm{A}/2},$$

$$= 1+\mathrm{D}/2 \cot \mathrm{A}/2,$$

D being the angle of deviation of the ray and A the refracting angle of the prism.

If μ is the refractive index of the vapour for the density ρ, and μ_0 the index for the standard density ρ_0, then we have

$$\frac{\mu_0-1}{\mu-1} = \frac{\rho_0}{\rho} \text{ and } \mu-1 = \tfrac{1}{2}\mathrm{D} \cot \frac{\mathrm{A}}{2},$$

or

$$\mu_0-1 = \frac{\rho_0}{\rho}\frac{\mathrm{D}}{2} \cot \frac{\mathrm{A}}{2},$$

D, the angle of deviation being measured in radius.

As in the case of the interferometer experiments, ρ_0 the standard density is given by

$$\rho_0 = \frac{\text{density of hydrogen at N.T.P.} \times \text{At. wt. of element}}{\text{molecular weight of hydrogen}}$$

$$= 0{\cdot}009001 \text{ grm./c.c. for mercury.}$$

If the deviation of the ray in seconds be denoted by δ, it follows that $\mathrm{D} = 4{\cdot}852 \times 10^{-6}\,\delta$, and substituting for D, in the formula given above,

$$\mu_0-1 = \rho_0/\rho \times 2{\cdot}426 \times 10^{-6} \,.\, \delta \,.\, \cot \mathrm{A}/2$$

$$= \rho_0/\rho \times 2{\cdot}288 \times 10^{-6}\delta, \text{ taking A to be } 93{\cdot}5^\circ.$$

In making these prism measurements, the furnace and the enclosed prism were maintained at a temperature of 320° C. The density of the saturated mercury vapour at this temperature was taken from Jewett's values to be 0·001988 grm./c.c. Monochromatic light from a mercury arc lamp of wave-lengths $\lambda = 4358{\cdot}56$ Å.U., $\lambda = 5460{\cdot}97$ Å.U., $\lambda = 5780$ Å.U., and $\lambda = 6234{\cdot}31$ Å.U., were used, the requisite radiations being obtained by the use of suitable Wratten and Wainwright filters.

As an indication of the magnitude of the measurements actually made, it may be stated that values were obtained for δ, for the different wave-lengths used which ranged from 83 to 91 seconds of arc. The values of the refractive indices deduced are given in the sixth column of Table III; it will be seen they are slightly lower than those obtained in the interferometer determinations. They are, however, sufficiently in agreement with the latter to demonstrate the feasibility of using the prism method.

6. *Prism Experiments with Thallium Vapour.*

In the experiments with thallium vapour, the procedure followed was identical with that adopted in dealing with the mercury vapour, sufficient metallic thallium being used to fill, when melted, the lower tube and part of the prism itself. As the densities of saturated thallium vapour for different temperatures have not as yet been determined, the determination of the refractive indices was confined to readings taken with a density corresponding to a temperature of 540° C. The melting point of thallium is 301° C., and it was found that, at the temperature selected, the density of the vapour was sufficient to give readings on the refractometer, which could be made with ease and accuracy. In all, the refractive indices were determined for eight wave-lengths, the radiations used being obtained either from the mercury arc lamp or from a Geissler tube containing hydrogen.

The indices, as determined, are given in the eighth column of Table III, and are shown graphically in fig. 3.

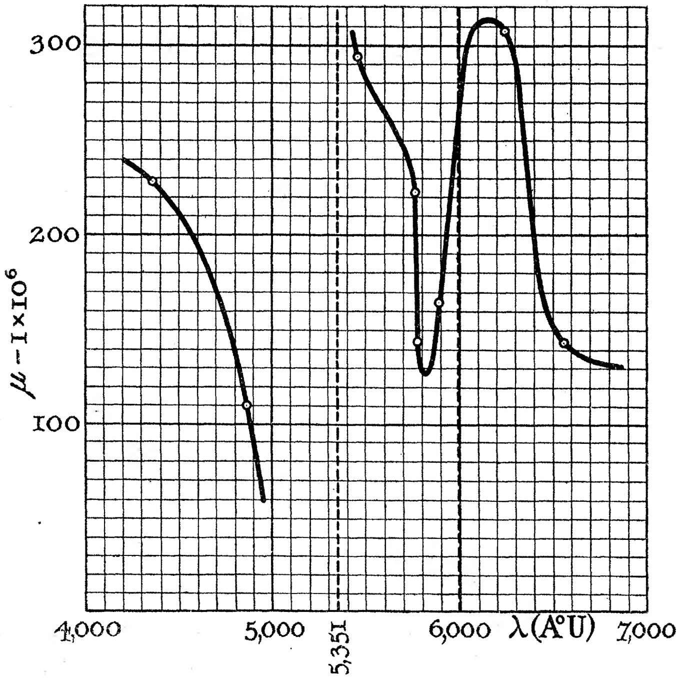

Fig. 3.

7. *Anomalous Dispersion with Thallium Vapour.*

From the form of the graph in fig. 3, it will be seen that anomalous dispersion is clearly indicated at the wave-length λ = 5350·65 Å.U., and probably also at or near the wave-length λ = 6000 Å.U. Direct experiments made by Guthrie[*] failed in showing any absorption of this wave-length by non-luminous thallium vapour. It is known, however, from the work of Kayser and Runge,[†] that the wave-length λ = 5350·65 Å.U. is strongly reversed in the arc spectrum of thallium, and Hermann Geisler[‡] has shown, too, that if light be passed through thallium, vapourised in the carbon arc, anomalous dispersion is obtained at this wave-length. The only direct observation of absorption by non-luminous thallium vapour at λ = 5350·65 Å.U. appears to be that obtained by G. E. Gibson[§] under very exceptional conditions. In his experiments, he found that carefully purified thallium, when sealed within an evacuated clear fused quartz tube, and then heated in an electric oven to 1300° C., emitted the thallium green line strongly. This he showed to be a pure temperature effect. When, however, with the electric oven at 1350° C., the cold tube containing the thallium was inserted in the oven, he found, a short time after introducing the tube, that the reversed thallium line 5460·65 Å.U. could be seen as a dark line on the continuous spectrum of the heated oven, which acted as a radiating black body.

From the experiments of Gibson, it would appear, therefore, that the anomalous dispersion indicated by the present investigation as existing at λ = 5350·65 Å.U. is very probably correct. It is not clear, however, why non-luminous thallium vapour, when tested directly by passing the light of a continuous spectrum through it, does not show absorption at λ = 5350·65 Å.U. It should also be stated that, up to the present, no investigator appears to have observed any absorption by non-luminous thallium vapour in the neighbourhood of λ = 6000 Å.U., and that the nearest wave-length to λ = 6000 Å.U. in the emission spectrum of thallium appears to be that observed by Eder and Valenta[‖] with the spark at λ = 5949·08 Å.U.

8. *Results.*

1. It has been shown that interferometer tubes and hollow prisms of clear fused quartz, free from distortion and all trace of devitrification, can be readily made by a new method.

2. With such tubes, determinations have been made of the refractive indices for a number of wave-lengths with the vapours of mercury and thallium.

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[*] Guthrie, 'Ast. Phys. Jl.,' vol. 29, No. 1, p. 211 (1909).

[†] Kayser and Runge, 'Wied. Ann.,' vol. 48, p. 126 (1893).

[‡] Hermann Geisler, 'Inaug. Diss. University of Bonn,' January 20, 1909.

[§] G. E. Gibson, 'Phys. Zeit.,' vol. 12, p. 1145, December 8, 1911.

[‖] Eder and Valenta, 'Wien. Ber.,' vol. 118, IIa, pp. 511, 1077 (1909).

3. The dispersion curve for non-luminous thallium vapour indicates the existence of anomalous dispersion at the wave-lengths $\lambda = 5350 \cdot 65$ Å.U., and probably also at or near the wave-length $\lambda = 6000$ Å.U.

In conclusion, I desire to express my great appreciation of the help given me by my students, Messrs. H. Grayson Smith and L. W. Rentner, in taking the readings, and to that given me by my assistant, Mr. R. H. Chappel, in making up the interferometer tubes and prisms.

On the Emission and Absorption Spectra of Mercury.

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[Plate 7.]

1. *Introduction.*

In two papers by Raymond C. Dearle* accounts are given of investigations in which a special study was made of the monochromatic radiation $\lambda = 1 \cdot 014\mu$. This radiation Paschen† found to be by far the strongest in the emission arc spectrum of mercury, and Dearle's observations corroborated this view.

Dearle found moreover, that when light of this wave-length was passed through non-luminous mercury vapour, even when of low density, a definite and well-marked absorption was obtained. He also found the same effect when the mercury vapour traversed was in direct contact with the mercury vapour in which the arc was established from which the original radiation was obtained, and was also directly illuminated by the radiation from this arc.

It is well known that the radiations whose frequencies are given by $\nu = (1 \cdot 5, \mathrm{S}) - (2, p_2)$, *i.e.*, $\lambda = 2536 \cdot 72$ Å.U. and $\nu = (1 \cdot 5, \mathrm{S}) - (2, \mathrm{P})$, *i.e.*, $\lambda = 1849 \cdot 6$ Å.U. are strongly absorbed by non-luminous mercury vapour, but no one as yet has been able to confirm the observations made by Dearle that the radiation $\nu = (2, \mathrm{P}) - (2 \cdot 5, \mathrm{S})$, *i.e.*, $\lambda = 1 \cdot 014\mu$ is absorbed by mercury vapour which is not luminous.

It is quite clear from the application of the quantum theory made by Bohr

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* Dearle, 'Roy. Soc. Proc.,' A, vol. 92, p. 608 (1916); vol. 95, p. 280 (1919).

† Paschen, 'Ann. der Phys.,' vol. 27 (13), p. 559 (1908).